



Crystal growth of titania by photocatalytic reaction

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ABSTRACT

Substrate plates coated with anatase-type titania thin films were immersed in a solution of titanium (IV) chloride and lithium nitrate at 353 K during UV irradiation. About 20 nm-sized anatase-type titania crystals were formed on the original titania film consisting of almost the same sized particles. Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the original titania film. The pH value increased on the titania surface, which caused the titanium hydroxide formation. The titanium hydroxide was then dehydrated and transformed into titania. The titania particles formed on the substrate exhibited a photocatalytic activity similar to the original titania.

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1. Introduction

Titania is one of the most important photocatalysts that is widely investigated by many researchers all over the world because it is highly stable and easy to prepare from commercially available materials [1,2]. The original titania can be transformed into visible light-active materials by certain chemical and physical doping techniques although it can absorb only UV light [2]. Its photocatalytic activity can be improved by surface modification of the original photocatalyst particles. Nanoparticles or nanoclusters of metal oxides are used as modifiers in order to increase the visible light activity, efficiency, and lifetime of the charge separation [3].

Zinc oxide particles were previously deposited from an aqueous solution of zinc nitrate at 323–358 K on a titania thin film by a photocatalytic reaction [4,5]. The zinc oxide films are also prepared by an electrodeposition [6–8] or electroless deposition [9–12] by chemical reactions. However, the photocatalytic reaction can control the amount and size of the deposited particles by changing the amount of the irradiated photons, suitable for forming nanoparticles on the original photocatalyst particles.

The amorphous or low crystalline zinc hydroxide aggregates were deposited at a low temperature. The zinc oxide crystals with about 1–2 μm -sized hexagonal columns and 10 nm-sized spheres were formed at 338–358 K. The formation process can be expressed as follows [13–15]: Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the titania film. The pH value increased on the substrate surface with the titania film, which caused the zinc hydroxide formation on the film. The zinc hydroxides were then dehydrated and transformed into zinc oxide. The average crystallite size of the zinc oxide decreased with an increase in the reaction temperature because the reaction rates of the formation and dehydration of the zinc hydroxides increased which resulted in an increase in the formation rate of the crystal zinc oxide nuclei.

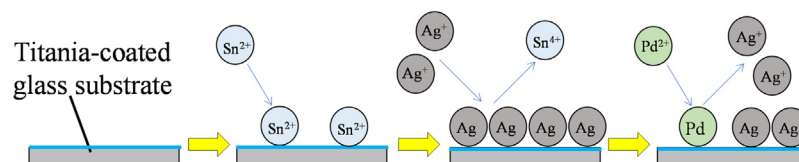
An electrodeposition and chemical deposition cannot easily produce anatase-type titania films due to difficulty in the reaction control. Photocatalytic reaction can produce active nanoparticles or nanoclusters of titania on the original titania particles. The titania growth is a model of formation of metal oxide nanoparticles as the modifiers which can improve the photocatalytic activity.

In this study, based on such a preparation method of zinc oxide, titania nanoparticles were also attempted to be formed from an aqueous solution of titanium (IV) chloride containing nitrate ions on a substrate plate with a titania thin film by a photocatalytic reaction. Titanium is easier to form its hydroxide than zinc and more difficult to be dehydrated. The activation energy of dehydration and

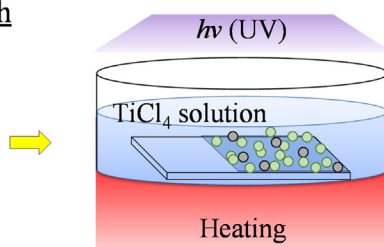
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Pretreatment (Ag and Pd particle formation)



Titania growth



Scheme 1. Diagrammatic illustration of pretreatment and titania crystal growth.

crystallization for titanium hydroxide (ca. 150 kJ mol⁻¹) is generally higher than that for zinc hydroxide (ca. 40–140 kJ mol⁻¹, depending on the coexisting anion) [16,17]. It is an important point that the dehydration of the titanium hydroxide can occur in the aqueous solution. We investigated the growth of the titania nanocrystals using its photocatalytic activity in order to apply the reaction conditions to the formation of the other metal oxide nanoparticles.

2. Experimental section

2.1. Materials

Titanium tetraisopropoxide, a titanium (IV) chloride solution, ethanol, 2-propanol, diethyleneglycol, polyethyleneglycol (M.W. = 20,000), nitric acid, hydrochloric acid, sodium hydroxide, tin (II) chloride, silver nitrate, palladium (II) chloride, and lithium nitrate (Wako, S or reagent grade) were used without further purification. Water was ion-exchanged and distilled by a distiller (Yamato WG23). The Ti plates (Takeuchi Kinzoku-Hakufun Kogyo), glass plates (Matsunami S-1111), and glass plates with ITO films (AGC Fabritech, 14 Ω cm⁻²) were used after washing with ethanol.

2.2. Sample preparation

The titanium metal, glass, and ITO glass substrates were coated with a very thin titania film by the sol-gel method. The sol was prepared by mixing 25.0 cm³ of ethanol, 0.21 cm³ of nitric acid, and 0.21 cm³ of water, then adding 5.0 cm³ of titanium tetraisopropoxide in a dry nitrogen atmosphere. The anatase-type titania films were prepared by three or ten dip-coatings using the sol, then heating at 773 K for 30 min. The thickness of the ten-layered film was ca. 300 nm. The substrates with the titania film were rinsed in 2-propanol and 0.10 wt% polyethyleneglycol aqueous solutions along with ultrasonication for 5 min each. Furthermore, they were rinsed in water with ultrasonication for 1 min, then immersed in 1.0 mol dm⁻³ hydrochloric acid containing 0.24 mol dm⁻³ SnCl₂ as the sensitizer, 4.4 mmol dm⁻³ AgCl as the first activator, and 5.9 mmol dm⁻³ PdCl₂ as the second activator for 10 min each. Sn²⁺ was adsorbed on the substrate surface, then substituted with Ag and Pd because Sn²⁺ reduced Pd²⁺. Consequently, Ag and Pd particles were formed on the surface as the nuclei for the titania crystal growth and as the promoter for the titania photocatalyst [4,5].

A material solution was prepared with 5.0 cm³ of the titanium (IV) chloride solution, 16.2 cm³ of water, 18.8 cm³ of 1.0 mol dm⁻³

hydrochloric acid, and 20 mmol lithium nitrate or nitric acid of which the pH value was ca. 6. The substrates were immersed in the material solution maintained at 353 K in the dark or during light irradiation using a high-pressure mercury lamp (SEN LIGHTS HB-100-A, 100 W) without stirring. The distance between the substrate and lamp was ca. 2 cm. After the irradiation for 4 h, the samples were washed with water, then dried at room temperature. Scheme 1 shows the diagrammatic illustration of the Ag and Pd particle formation and the titania crystal growth.

2.3. Measurements

A Micromorphology study of the samples was done using a field emission scanning electron microscope (FE-SEM, Hitachi SU8000). The X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku SmartLab). The UV-vis absorption spectra were measured using a spectrophotometer (Shimadzu UV-3150). The Fourier transform infrared-reflection absorption spectroscopy (FTIR-RAS) for the film samples were conducted using an FTIR spectrophotometer (Shimadzu IRPrestige-21) with an RAS accessory. The X-ray photoelectron spectroscopy (XPS) was conducted by AlK α radiation using an X-ray photoelectron spectrophotometer (Shimadzu/Kratos AXIS-HS3.5). For examination of the photocatalytic properties, the samples were prepared on the ITO glass substrates by the method described above. The electrolyte solution consisting of diethyleneglycol containing 0.50 mol dm⁻³ LiI and 50 mmol dm⁻³ I₂ was allowed to soak into the space between the sample and the counter Pt electrode. The samples were irradiated using monochromatic light generated by a fluorescence spectrophotometer (Shimadzu RF-5300) equipped with a Xe short arc lamp. During the light irradiation, the short circuit current was measured in the range from 350 to 400 nm by a digital multimeter (ADC 7461A).

3. Results and discussion

3.1. Titania crystal growth during UV irradiation

The material solutions became turbid after the UV irradiation. The particle formation can occur not only on the substrate surface, but also in the solution. The XRD patterns of the substrate and precipitates were observed in order to identify the reactions and products. Fig. 1 shows the XRD patterns of the Ti substrate with the very thin titania foundation film and that on which the film

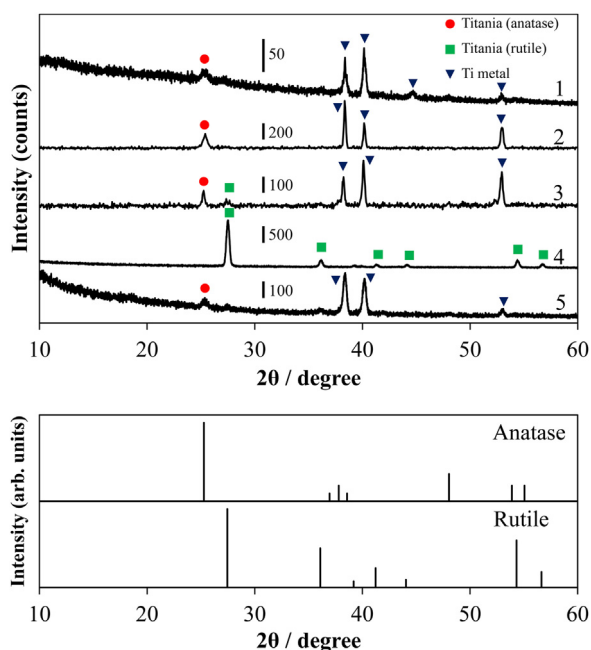


Fig. 1. XRD patterns of the Ti substrate with (1) the very thin titania film and that on which (2) the film was prepared from the titanium (IV) chloride solution with lithium nitrate during UV irradiation, then heated at (3) 773 and (4) 1073 K for 1 h and (5) that stored in the dark. TiO_2 (anatase): ICDD PDF 21-2172, TiO_2 (rutile): ICDD PDF 21-1276.

was prepared from the titanium (IV) chloride solution with lithium nitrate during the 4-h UV irradiation, then heated at 773 and 1073 K for 1 h and that stored in the dark. The anatase-type titania pattern was observed on the substrate surface before the irradiation. The peak intensity relatively increased by the irradiation time whereas the pattern slightly changed in the dark. This indicated that the anatase-type crystalline particles grew due to the UV irradiation. The anatase phase was transformed into a rutile phase at more than 773 K. The size of the anatase-type titania crystallites of these films was estimated from their full-width at half-maximum of the 25.3° peak using Scherrer's equation. The crystallite size for the film before and after the UV irradiation, then after heating was 22, 21, and 47 nm, respectively.

Fig. 2 shows the XRD patterns of the precipitates formed during the irradiation and in the dark. Broad peaks due to rutile phase were observed for the precipitates formed during the UV irradiation and in the dark. The crystals grew by heating the precipitates at 1073 K for 1 h. The rutile phase was also produced without UV irradiation or titania foundation. The pH values in the bulk solution were 3.69 and 3.85 before and after the 4-h UV irradiation, respectively, i.e., it was slightly changed by the irradiation. It was also reported that complex ions, $[\text{Ti}(\text{OH})_m\text{Cl}_n]^{2-}$, formed under the acidic conditions were easily transformed into the rutile structure [18]. These results indicated that different reactions occur in the solution and on the substrate surface. Titanium hydroxide was formed on the basic substrate surface, then thermally dehydrated during the UV irradiation. Lithium compounds were not observed on the substrate surface or in the precipitates even after heating at 1073 K although the material solution contained lithium ions. This is because the deposition of the titanium oxide precursor particles was so fast that the titanium ions could not react with the base metal ions, i.e., lithium ions, under the present conditions, whereas it was reported that the lithium titanate precursor as a neutralization salt was thermally formed in the solution [19].

Fig. S1 shows the XRD patterns of the glass substrate with the very thin titania foundation film and that on which the film was pre-

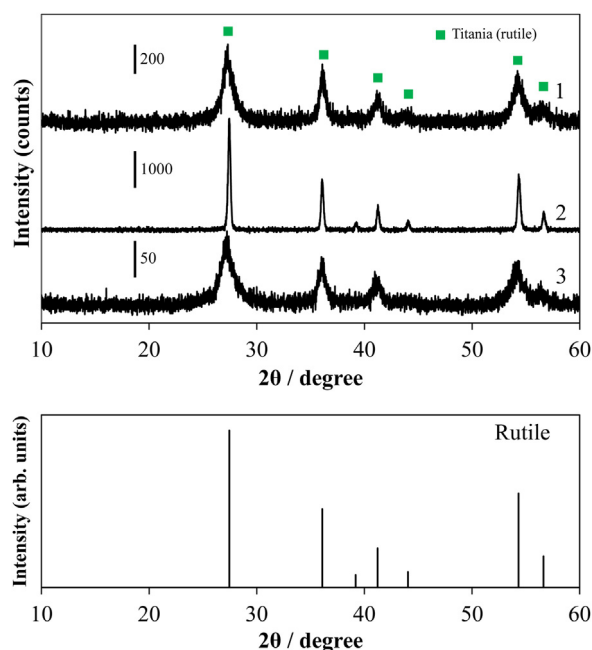


Fig. 2. XRD patterns of the precipitates formed (1) after the irradiation, then (2) heated at 1073 K for 1 h and (3) in the dark. TiO_2 (rutile): ICDD PDF 21-1276.

pared from the titanium (IV) chloride solution with lithium nitrate during the UV irradiation. The anatase-type titania crystals grew during the UV irradiation similar to those growing on the Ti substrate although the rutile titania was slightly deposited from the solution.

The SEM images of the surface and cross section of the samples prepared on the Ti substrates are shown in Fig. 3. The original titania film on the Ti substrate consisted of about 20 nm particles. Almost the same-sized particles were observed on the deposited film surface. The film thickness definitely increased from 300 ± 20 nm to 350 ± 10 nm by the irradiation. Therefore, the reactions on the substrate surface and in the solution were clearly different. The lithium ions did not react on the substrate's surface. The anatase-type crystal did not grow without the UV light or titania foundation. Fig. S2 shows SEM images of the cross section of the samples prepared on the glass substrates. The surface of the film deposited during the UV irradiation was found to be rougher than the original surface of the titania foundation. This indicated that a new layer was formed by the heterogeneous nucleation.

Similar to the zinc oxide formation [13–15], nitrate ions were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the original titania film. The pH value increased on the titania surface, which caused the titanium hydroxide formation in the presence of titanium ions. The anatase-type titania crystals formed after the titanium hydroxide were dehydrated. However, there is the possibility that the some particles remained as amorphous titanium hydroxide under the present conditions surrounded by water. Fig. 4 shows the FTIR spectra of the as-deposited samples, then heated at 773 K. All the spectra have the TiO stretching vibrational peak at around 840 cm^{-1} [20–22]. The as-deposited sample exhibited the OH stretching and bending vibrational peaks at around 3200 and 1600 cm^{-1} , respectively, assigned to the OH group and the adsorbed water [23–26]. The band at around 1400 cm^{-1} due to the adsorbed nitrate or nitrite ions was also observed in the as-deposited sample [27]. The relative intensities of these peaks decreased with an increase in the heating temperature. This result indicated that some of the titanium hydroxide deposited from the solution remained at a low tempera-

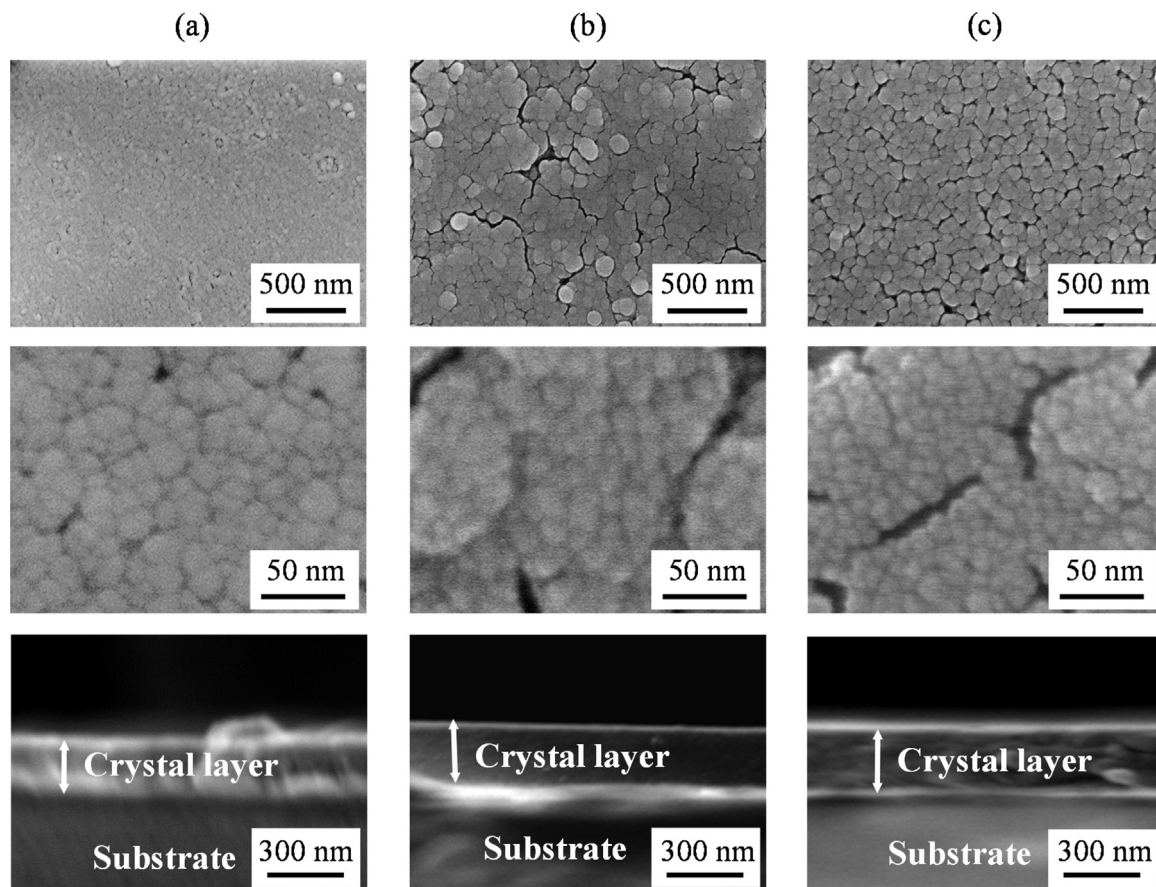


Fig. 3. SEM images of the surface and cross section of the Ti substrate with (a) the very thin titania film and that on which (b) the film prepared from the titanium (IV) chloride solution with lithium nitrate during UV irradiation, then (c) heated at 773 K for 1 h.

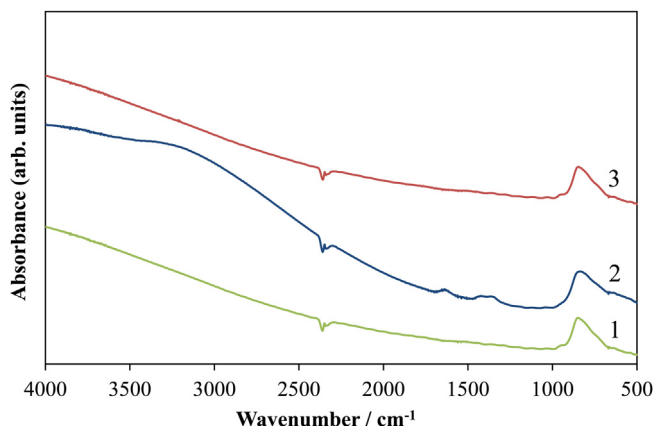


Fig. 4. FTIR spectra of the Ti substrate with (1) the very thin titania film and that on which (2) the film prepared from the titanium (IV) chloride solution with lithium nitrate during UV irradiation, then (3) heated at 773 K for 1 h.

ture because the thermal energy was not high enough to completely dehydrate it.

Fig. S3 shows the XPS spectra related to the binding energy of the Ti 2p and O 1s electrons for the glass substrate sample before and after the UV irradiation. The Ti 2p spectra of both samples exhibited peaks at 464.3 and 458.6 eV, assigned to the typical Ti^{4+} [28–30]. The O 1s peaks were observed at 529.8 eV in the untreated sample, assigned to the lattice oxygen of the titania crystal. The irradiated sample also exhibited a band at around 532–533 eV, assigned to the OH group and adsorbed water [26,29–31]. This corresponds to the FTIR spectra in Fig. 4.

Fig. S4 shows the XRD patterns of the substrate with the very thin titania film and that on which the film was prepared from the with “nitric acid” instead of “lithium nitrate” during UV irradiation, then heated at 773 and 1073 K for 1 h. Anatase titania grew on the titania foundation by the photocatalytic reaction and annealing, followed by the phase transition into rutile at a higher temperature. This result was similar to that using lithium nitrate. The lithium ions did not play an important role in the reactions on the substrate.

3.2. Photocatalytic activity

The methylene blue degradation and photocurrent measurements were conducted in order to examine the photocatalytic activity of the prepared samples. Fig. 5 shows the amount of the methylene blue degraded by the UV irradiation and photocurrent spectra for the substrate with the original titania film, the prepared sample as deposited, and that heated at 737 K. The degradation amount of methylene blue and the photocurrent value using the samples as prepared by the UV irradiation were similar those using the original titania substrate. The titania film consisting of amorphous or low crystalline particles produced a much lower photocatalytic activity and photocurrent [30,32]. The thermal and hydrothermal treatment significantly enhanced the activity [30,32,33]. As mentioned above, the crystallite size for the original titania film, the prepared sample as deposited, and that heated at 737 K was 22, 21, and 47 nm, respectively. The high crystallinity can increase the photocatalytic activity. The steam-treated sample consisting of the low crystalline titania particles exhibited a 70% activity compared to the heated sample [30]. It was suggested that the electrons can be transported on the particle surface

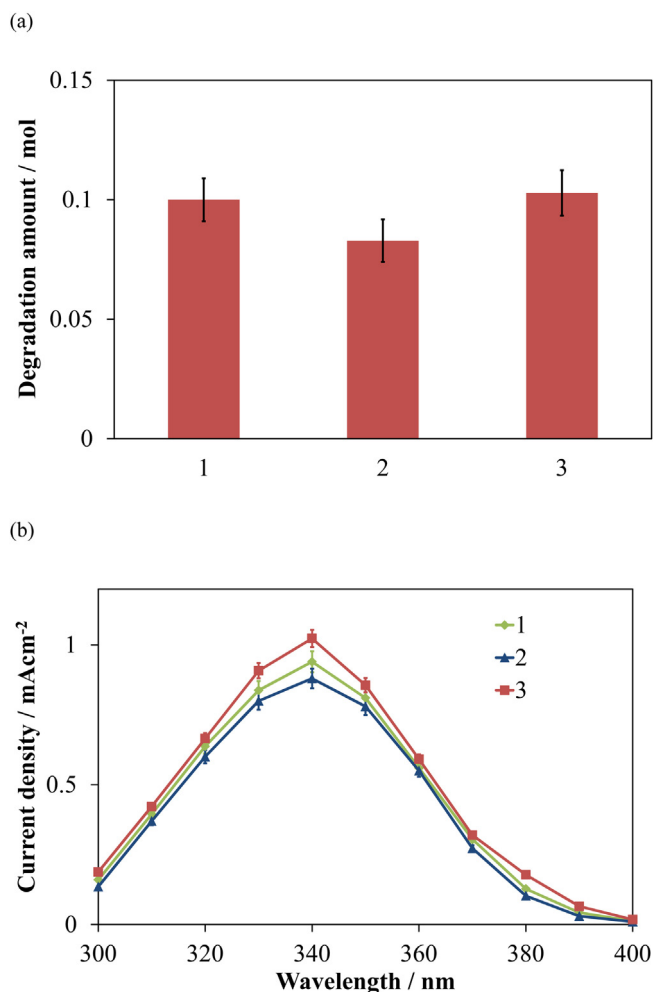


Fig. 5. (a) Amount of the methylene blue degraded during the UV irradiation and (b) photocurrent spectra for the ITO glass substrate with (1) the very thin titania film and that on which (2) the film prepared from the titanium (IV) chloride solution with lithium nitrate during UV irradiation, then (3) heated at 773 K for 1 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in such a low crystalline titania. The activity definitely increased after heating at 773 K corresponding to dehydration of the titanium hydroxide. The titanium hydroxide exhibited a low activity and prevented the charge separation and electron transport. It is important that the rate of the dehydration was accelerated versus that of the titanium hydroxide formation on the substrate to form the photocatalytically active titania.

4. Conclusions

Titania nanoparticles were formed from an aqueous solution of titanium (IV) chloride containing nitrate ion on a substrate plate with the original titania thin film at 353 K by a photocatalytic reaction. The anatase-type titania crystals with about 20 nm-sized spheres were formed on the original titania film consisting of almost the same sized spherical particles. Nitrate ions in the solution were reduced to nitrite ions, and water was transformed into hydroxide ions by a photocatalytic reaction on the original titania film. The pH value increased on the substrate surface with the film, which caused the titanium hydroxide formation on the film. The titanium hydroxide was then dehydrated and transformed into titania because the substrate surface was heated by the irradiation. The titania particles formed on the substrate exhibited a photocat-

alytic activity similar to the original titania. However, the titanium hydroxide partly remained in the compounds formed on the substrate. The activity was improved by annealing at 773 K, which promoted the dehydration of the titanium hydroxide.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: [10.1016/j.apcatb.2017.05.076](https://doi.org/10.1016/j.apcatb.2017.05.076).

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